THESIS.

THE DETERMINATION OF NEUTRAL EQUIVALENTS OF FATTY ACIDS.

and

BINARY SYSTEMS OF SOME FATTY ACIDS.

and

THE PREPARATION AND DECOMPOSITION OF p-METHOXY-PHENYL o-CHLORO-PHENYL IODONIUM BROMIDE: A METHOD OF ESTABLISHING THE RELATIVE DEGREE OF ELECTRONEGATIVITY OF ORGANIC RADICALS.

Submitted in Partial Fulfilment of the Requirements for
the Degree of Master of Science.

BY

Marshall Kulka B. Sc.

Under the direction of Dr. R. B. Sandin.


UNIVERSITY OF ALBERTA
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Time devoted to thesis work: 5.3 months out of seven
months devoted to M. Sc. work.

Time is proportioned on basis of 7.0 months for an
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THE DETERMINATION OF NEUTRAL EQUIVALENTS OF FATTY ACIDS.

Ordinary titration in the determination of neutral equivalents of fatty acids has proven to be far from satisfactory. The amount of fatty acid required in the determination is large, making it wasteful, which is a detriment to fatty acid research. The work on fatty acids in this laboratory [1] has shown it to be also desirable that a more suitable method be devised.

The use of ethyl alcohol as a solvent in acid - base titrations in this particular work, is advantageous for two reasons. The first is its solvent power on fatty acids and their soaps, the latter being not very soluble in water. The second is the somewhat greater sharpness of the end point obtainable.[2] This is due to the fact that the dissociation of alcohol is much less than that of water, so that there is a greater range of hydrogen ion concentration between an acid and an alkaline solution. For the same reason the

degree of alcoholysis of salts of weak acids and bases is less than the degree of hydrolysis, consequently the change in hydrogen ion concentration through the end point is more rapid in alcohol than in water. The bases in the alcohol system are ethylates, so that the neutralization of a weak acid by sodium ethylate would be represented in the ionic form by the equation,

$$HA + C_2H_5\bar{O} \rightarrow \bar{A} + C_2H_5OH.$$

While the dissociation of the acid HA is doubtless smaller in alcohol than in water, the dissociation of the alcohol is so much less than that of water, so as to account for the degree of alcoholysis just mentioned. The alcoholysis of the salt is, of course, represented by the reverse equation.

For the titration of weak acids and bases, it is necessary to select an indicator which changes color at the hydrogen ion concentration existing at the true end point, when the acid and the base are present in equivalent quantities.[3] An indicator scale [4] for alcoholic solutions, similar to those in common use for aqueous solutions, has been prepared. The

indicator which changes color at the hydrogen ion concentration existing at the true end point in the titration of fatty acids with sodium ethylate, is thymolphthalein.

The purpose of this investigation, therefore, has been the determination of neutral equivalents of fatty acids by titrating in ethyl alcohol with the ethylate ion as the base. Much smaller quantities of the fatty acids, than is customary have been used. To make the end point more visible, Nessler tubes and a mixed indicator have been used.

MATERIALS.

ETHYL ALCOHOL[4] - Ninety-five per cent ethyl alcohol was distilled from concentrated sulfuric acid to remove amines (10-15 cc. of concentrated sulfuric acid to one liter of alcohol). It was distilled again from silver nitrate and potassium hydroxide to remove aldehydes (10 g. per liter of silver nitrate and a little potassium hydroxide). Then it was left in contact with calcium oxide for two days and finally redistilled using a trap to prevent any solid material distilling over.

SODIUM ETHYLATE - After bubbling hydrogen gas through the ethyl alcohol, enough sodium was added to make the solution about 0.05 N.

FATTY ACIDS - Eastman Kodak Company fatty acids were recrystallized from acetone until a constant capillary melting point was obtained, and agreed with those found in the literature.[5] After six recrystallizations from acetone fifty grams of the Eastman product gave twenty grams of the pure fatty acid in the case of stearic and palmitic acids. Fifty grams of myristic acid, after four recrystallizations, gave ten grams of the pure acid. Fifty grams of lauric acid, after three recrystallizations gave six grams of the pure acid. All the fatty acids were dried in an Abderhalden dryer, using concentrated sulfuric acid as the drying agent, water as a heating liquid, and with the system evacuated. The temperature was high enough to melt the fatty acid, and it was kept in the molten condition for at least two hours.

BENZOIC ACID - Bureau of Standards benzoic acid was dried in an Abderhalden dryer in a similar manner to

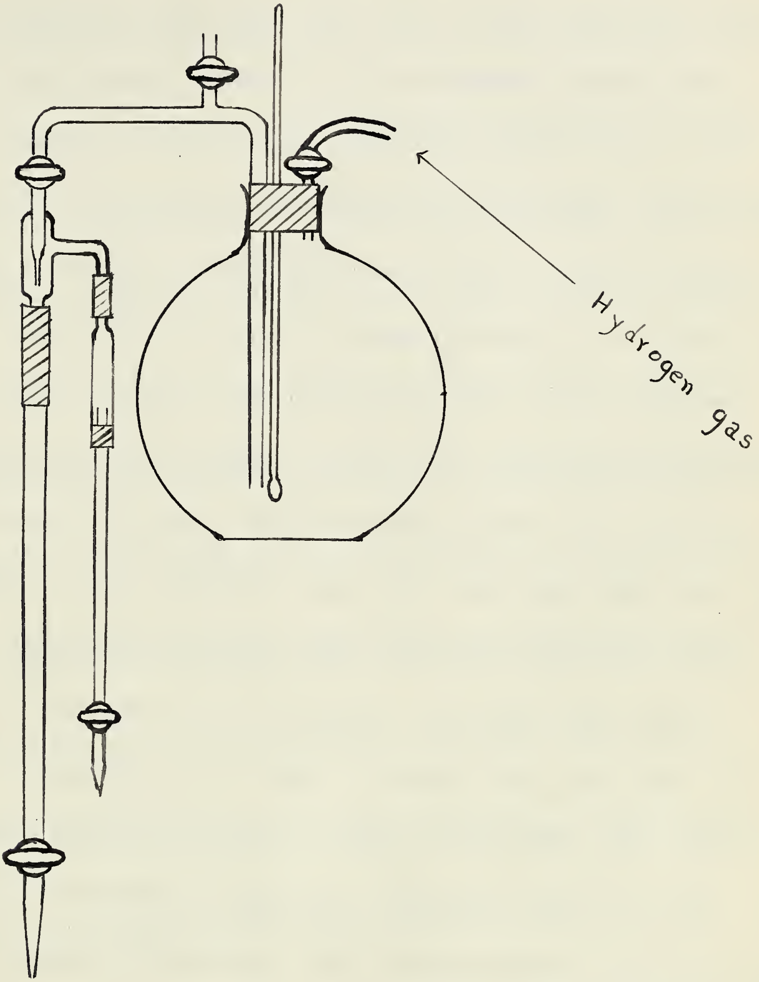
that of the fatty acids.

THYMOLPHTHALEIN INDICATOR - Five grams of thymolphthalein was dissolved in a liter of alcohol.

APPARATUS.

(See page 6 for diagram).

The sodium ethylate was kept in a three liter short-necked flask under an atmosphere of hydrogen furnished by a Kipp generator. The hydrogen was purified by passing through alkaline pyrogallol to remove oxygen, silver nitrate to remove arsine, soda lime to remove carbon dioxide, and finally through calcium chloride to remove water vapor. The micro-burette was filled by the pressure of hydrogen forcing the sodium ethylate up the tube into the burette. It was found necessary to completely empty the burette after the end of a titration, because if left in, the sodium ethylate dissolved off the stopcock grease, and air was admitted into the system, which caused the sodium ethylate to become colored yellow. This is due to the fact that oxygen oxidizes the alcohol to the aldehyde and then in the presence of alkali there is polymerization.


Hydrogen gas

PROCEDURE.

The fatty acid was weighed out into Nessler tubes. An amount equivalent to about ten cc. of 0.05 N sodium ethylate was used. Ten cc. of the purified ethyl alcohol was added to each of the Nessler tubes from a pipette taking care to wash down any particles of the fatty acid clinging to the walls of the tube. Five drops of thymolphthalein indicator and three drops of methyl orange indicator (0.2 g. of methyl orange per liter of water) were added to each of the tubes. Each Nessler tube was heated to about sixty-five degrees centigrade, by running hot water, and titrated with 0.05 N sodium ethylate. A ring stirrer was used and when near the end point, vigorous stirring was required after the addition of each drop. One Nessler tube was used as a control. Twenty cc. of ethyl alcohol was put into it, and three drops of methyl orange indicator. The solution being titrated, remained the same color as the control during titration. At the end point the solution being titrated became a darker color than the control. The color change is from a yellow to a blue and is quite distinct with the addition of one drop of the sodium

ethylate.

EXPERIMENTAL.

The sodium ethylate was standardized against Bureau of Standards' benzoic acid. About 0.06 g. of benzoic acid was weighed out into a Nessler tube, and titrated in the same manner as described above. In the earlier titrations no auxiliary indicator was used, the thymolphthalein alone acted as indicator. Since the end point was not very visible, especially in the absence of good daylight, it was difficult to obtain good results. Therefore it was necessary to do many titrations before the skill in observing the end point was acquired.

Sixteen samples each of stearic and of palmitic acids were titrated, and in each case not more than 0.15 g. of the fatty acid was used. Thymolphthalein alone as indicator was used. Under the same conditions, fourteen different mixtures of palmitic and stearic acids were titrated, giving the following results.

NEUTRAL EQUIVALENTS.

TABLE (1).

Pure Stearic Acid	Pure Palmitic Acid	Mixtures % Stearic	Experimental Neutral Equivalents	Calculated Neutral Equivalents
284.7	257.6	7.97	257.0	258.3
284.0	255.6	9.59	258.6	258.9
284.3	257.0	21.26	261.2	262.3
284.4	256.7	21.54	263.7	262.4
283.6	256.7	23.56	262.1	262.7
284.8	256.4	23.67	264.0	262.8
285.2	256.5	35.58	265.5	266.2
284.1	256.4	37.70	267.0	266.8
284.4	256.1	53.45	271.7	271.1
283.9	256.9	54.31	271.0	271.5
284.5	256.5	66.02	275.2	274.8
280.3	256.6	66.93	275.7	275.0
281.9	255.1	84.55	279.2	279.2
283.1	256.7	84.84	279.3	280.0
283.4	256.3			
	256.1			
284.3	256.3	(Calcd).		

The last four on stearic acid were done by electric light and are not so good. It is seen that the neutral equivalents of fatty acids can be determined with an error of 0.5 %, providing titrations are done in good daylight. The composition of a binary mixture can also be determined in the same way.

Another factor to be controlled, was the change of volume of the sodium ethylate with temperature. The volume change of 10 cc. of ethyl alcohol is 0.01 cc.

per degree change of temperature. Therefore it became necessary to standardize the sodium ethylate before every series of titrations and to keep the temperature as constant as possible. If any change of temperature occurred during the titration, corrections were applied. The results with this controlled factor are as follows:

TABLE (2).

Percent Stearic	Experimental Neutral Equivalents	Calculated Neutral Equivalents
0.0	256.2	256.3
100.0	284.4	284.3
11.11	259.2	259.3
24.65	261.9	263.0
37.75	265.5	266.9
50.00	268.3	270.2
64.89	273.4	274.4
77.09	276.3	277.9
83.97	278.8	279.3

Again the error is the same as before but the calculated values are all higher than the experimental values.

Since only 0.06 g. of benzoic acid was used in the standardization of the sodium ethylate, it was thought that this weight and the low equivalent of benzoic acid might have something to do with this error.

Therefore the sodium ethylate was standardized against stearic acid and then mixtures of stearic and palmitic acids were titrated. The results obtained are shown in Table (3).

TABLE (3).

Percent Stearic	Experimental Neutral Equivalents	Calculated Neutral Equivalents
0.0	256.6	256.3
5.7	258.1	257.9
19.36	261.1	261.5
32.55	265.5	265.4
44.74	268.9	269.9
56.89	271.6	272.2
77.94	278.8	279.1
53.65	271.4	271.3
65.24	274.5	274.5
47.97	270.2	269.7
33.88	264.4	265.6
14.33	259.5	260.3
10.87	253.8	259.2
23.71	262.7	262.7
39.04	266.8	267.2
45.23	268.7	269.0
54.53	270.0	271.5
Palmitic	256.1	256.3

The error is somewhat smaller than before but not appreciably. Therefore the error introduced when using benzoic acid for standardizing the sodium ethylate is not responsible for the total error in the neutral equivalents.

Since the effect of light on the end point is marked, it became necessary to use a constant source of light. A daylight lamp was set up and a series of titrations made using benzoic acid for standardizing the sodium ethylate. The results are shown in Table (4)

TABLE (4).

Palmitic Acid	(Mixtures of Palmitic and Stearic Acids)		
	Percent Stearic	Experimental Neutral Equivalents	Calculated Neutral Equivalents
258.1	16.10	261.3	260.8
256.8	41.83	267.7	267.7
256.0	37.80	267.1	266.8
256.0	64.40	273.0	274.2
256.3	78.74	277.9	278.4
256.7	96.20	280.4	281.5
256.3 (Calcd)			

During the course of these titrations it was observed that the end point was not as distinct as in ordinary daylight. The results also show that a daylight lamp is valueless.

A final run was just about to be made when the sodium ethylate became colored yellow. A set of titrations were done using the colored solution standardized against benzoic acid.

TABLE (5).

TITRATIONS USING COLORED SOLUTION OF SODIUM ETHYLATE.

(Mixtures of Stearic and Palmitic Acids).

Percent Stearic	Experimental Neutral Equivalents	Calculated Neutral Equivalents
9.56	258.0	258.8
34.28	265.7	265.7
50.06	270.3	270.3
58.21	271.4	272.5
71.46	276.5	276.4
83.80	279.2	279.7

Stearic Acid	Palmitic Acid	Myristic Acid	Lauric Acid
284.1	256.2	227.2	199.6
284.0	255.8	228.2	199.0
284.2	255.7	227.9	199.6
283.6	255.5		
284.2	256.1	228.2(Calcd.)	200.2 (Calcd.)
284.0	256.0		
283.9	256.0		
284.2	256.4		

During the titration, it was observed that the end point was much sharper and more visible than the end point obtained when titrating with a clear solution of sodium ethylate. The results obtained are better than before. This immediately suggested mixed indicators. A mixture of thymolphthalein and phenolphthalein gave a very indistinct end point, but a mixture of thymolphthalein and methyl orange gave a very distinct end

point. Five drops of thymolphthalein (5 g. per liter of ethyl alcohol) and three drops of methyl orange (.2 g. per liter of water) were used.

TABLE (6).

TITRATIONS USING METHYL ORANGE AS AUXILIARY INDICATOR.

Neutral Equivalents Of:

Stearic Acid	Palmitic Acid	Myristic Acid	Lauric Acid
285.0	256.5	228.8	200.5
284.7	257.2	228.5	200.1
284.5	256.4	228.2	200.2
284.3(Calcd.)	256.2(Calcd.)	228.2(Calcd)	200.2(Calcd.)

The myristic and lauric acids were titrated at night by electric light and the end point was observable as well as in the daylight. From the results that it gave, and the sharpness of the end point, it was concluded that a mixed indicator of thymolphthalein and methyl orange was the most suitable for titrating fatty acids.

Attempts were made to do titrations in the butylate and the isopropylate systems but with little success. The fatty acids are more soluble in these alcohols but the soaps formed are not very soluble.

Finally an attempt was made to make the method

semi-micro by using not more than fifty milligrams of the fatty acid and titrating with 0.017 N sodium ethylate standardized against stearic acid. The following results were obtained.

TABLE (7).

RESULTS OF SEMI-MICRO TITRATIONS.

Palmitic Acid	Myristic Acid	Lauric Acid
258.3	229.3	200.0
257.5	230.0	200.9
257.0	227.8	200.3
255.2	227.0	201.0
	227.4	199.7
		200.6
256.3 (Calcd.)	228.2 (Calcd.)	200.2 (Calcd.)

This time the end point was not as sharp as before, two drops of sodium ethylate being required to give a distinct color change.

CONCLUSIONS.

A method has been devised to determine the neutral equivalents of fatty acids to within an accuracy of 0.4 % using at the most 0.15 g. of the fatty acid, or to within an accuracy of 0.6 % using semi-micro quantities or not more than .04 g. of the fatty acid. A mixed

indicator of thymolphthalein and methyl orange was found to be most suitable.

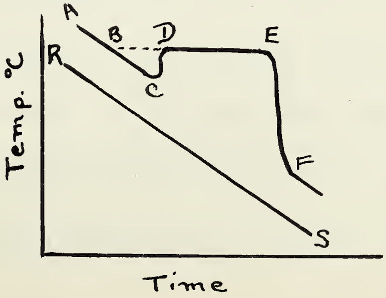
PART TWO.

BINARY SYSTEMS OF SOME FATTY ACIDS.

This work is a continuation of a systematic study of fatty acids and synthetic fats begun by Woolley and Sandin.[1] A study of binary systems of fatty acids is of importance from the standpoint of its possible analytical values, the separation of fatty acids from mixtures of these acids, and also from the standpoint of purely theoretical interest.

The purity of a fatty acid can be studied and confirmed with definite limitations by means of the cooling curve, i. e. the time - temperature curve. The form of the time - temperature curve for a single pure substance is given in fig. 1, the dotted portion at B representing the limiting case of no undercooling before freezing sets in.

(fig. 1)



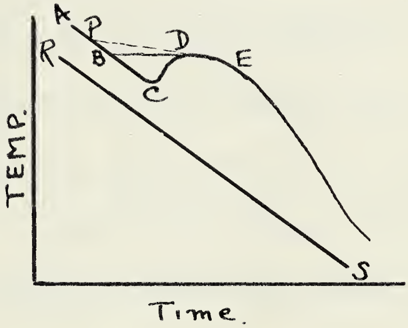
The temperature of a mass of a pure liquid, surrounded by a shield, cooling at a uniform rate (along RS), falls along the line AB to C at which point crystallization is initiated. The heat supplied by the crystallization raises the temperature to that of the true equilibrium between solid and liquid; and the curve is horizontal along DE. When crystallization is substantially complete, at E, the effective temperature head is relatively large, and so the mass at first cools rapidly; but finally the curve at F again becomes parallel to RS.

The shape of the curve described above is a good criterion of purity of a substance. With a perfectly pure sample, the temperature remains quite constant during the freezing (DE fig. 1); over an interval of five minutes or more. If the substance contains admixed impurity, the initial temperature of freezing will likely be depressed, the temperature falls off as the freezing progresses, and the concentration of the impurity in the solution increases. White [6] has given a thorough discussion of this matter, and its usefulness as a means of estimating the amount of impurity.

The interpretation of a time - temperature

curve for a binary mixture is as follows. A binary mixture cools similarly along AP (fig. 2) until one of the components begins (in the absence of undercooling) to separate at P, when there is a change in direction (along the curve PD), but there is no horizontal portion in the curve. The heat set free now causes the rate of cooling of the melt to change in a perfectly definite way, because to any temperature below P, there corresponds a definite composition of the residual liquid. Hence a definite amount of the component has crystallized, and a definite total amount of heat has been disengaged. The composition of the residual liquid approaches that of the eutectic, as the eutectic temperature is approached. At that temperature, the liquid still remaining, behaves like a pure substance. In this case, therefore, the

(fig. 2)



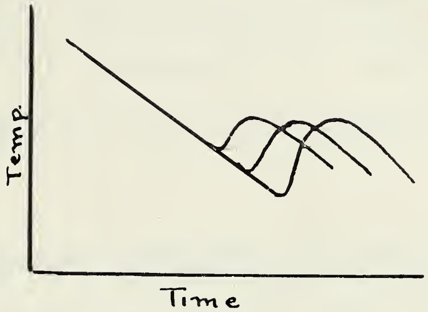
momentary composition of the solution is a factor in the cooling curve and its interpretation.

The typical experimental curve for a binary mixture differs only in that some undercooling is unavoidable and, indeed, not undesirable provided that the curve be interpreted properly. When crystallization is induced at C (fig. 2), equilibrium between component X and the solution is soon attained and maintained thereafter. The heat set free raises the temperature rapidly to a maximum D beyond which it falls off as before, a state of equilibrium being maintained. It is clear that the composition of the liquid phase at D differs from that of the original solution by the proportion of X which has then crystallized; and in careful work this fact must be properly taken into account. The usual methods of making this correction are not based upon sound principles and are unsatisfactory.

Bell and Herty [7] made this correction in the following way. They considered the initial portion of the graph (fig. 2), DE to be linear, producing it backwards to meet AB and assuming that this intersection represents the temperature corresponding to the initial

crystallization of X from the given solution. Now with different degrees of undercooling of a single solution, this procedure leads to different values, as is evident from fig. 3, and is therefore unsatisfactory. Moreover,

(fig. 3)



with solutions initially near the eutectic point, the curvature of the portion DE is so great as to render back extrapolation very uncertain if not impossible. The approximate character of this method of extrapolation has been remarked in two papers.[8] In this work, the freezing point was taken to be that at D (fig. 2) since with a small degree of undercooling the error is negligible.

The purpose of this investigation was to determine the freezing points of binary mixtures of the fatty acids-- stearic, palmitic, myristic, and lauric.

Work has been done on stearic - palmitic, margaric - stearic, and margaric - palmitic.[5] Compound formation between two fatty acids has been reported for mixtures of palmitic - stearic,[5] n eicosanic - stearic,[9] lignoceric - stearic and lignoceric - palmitic.[10] Compound formation has also been reported between lauric and palmitic acids.[11] No information is available on the behavior of mixtures of the other fatty acids.

MATERIALS, APPARATUS, AND PROCEDURE.

The purest Eastman Kodak Company fatty acids were used. These were recrystallized from acetone many times, and with a considerable loss, until a constant capillary melting point was obtained. Stearic and palmitic acids, after six recrystallizations from acetone gave a constant melting point. The loss in each case was fifty percent. Myristic acid required four recrystallizations from acetone to give a constant melting point. The loss in the myristic acid was eighty percent. Lauric acid gave a constant capillary melting point after three recrystallizations from acetone. The loss in this case was eighty-eight percent. The neutral

equivalents of these purified fatty acids agreed closely with the calculated values.

The determination of freezing points is best carried out by means of taking time - temperature curves. The most suitable way is by means of a thermoelement.[12] A suitable thermoelement was devised, but a sensitive enough galvanometer was not available, therefore it was necessary to resort to simpler apparatus. The form of apparatus finally used, was the ordinary molecular weight apparatus. A small test tube was surrounded by a larger one, forming an air jacket, and the whole was immersed in a water bath. The fatty acid (about one gram) was weighed out into a small test tube, the inside test tube in the set-up, and warmed until it all melted. A tiny stirrer and a thermometer (Unter Aufsicht der Physikalisch Technischen Reichsanstalt) calibrated to 0.1° were placed into the melted fatty acid. The test tube with the fatty acid, thermometer, and stirrer, was placed into the air jacket which was immersed in the water bath, the temperature of which was not more than three degrees below that of the liquid fatty acid. A

mechanical stirrer kept the water at a uniform temperature throughout, and a calibrated thermometer recorded its temperature. The whole was allowed to cool, and while stirring, the time and temperature at every half minute was recorded. The temperature fell gradually until supercooling induced crystallization. Precautions were taken to prevent excessive supercooling, otherwise the heat set free would not suffice to bring the temperature to the equilibrium point, and to compensate for the losses of radiation. The maximum to which the temperature rose after the beginning of crystallization was taken as the freezing point of the substance. Then mixtures of two fatty acids were made up and their freezing points determined in a similar manner. Each freezing point given is the result of several readings, and the maximum error in the reproduction of the freezing points was 0.05°. It should be noted that the freezing points in Tables (1) - (6) represent definite temperatures and are quite different from the usual capillary melting point ranges which are ordinarily quoted as criteria of purity.

FREEZING POINTS OF BINARY MIXTURES.

TABLE (1).

Data plotted in Curve (1).

Palmitic Acid Mol %	Stearic Acid Mol %	Freezing Point °C.
0.0	100.0	68.9
9.97	90.03	66.7
30.16	69.84	61.7
47.87	52.13	56.2
50.00	50.00	56.1
69.52	30.48	54.7
72.48	27.52	54.9
78.00	22.00	55.6
90.90	9.10	59.0
100.0	0.0	62.2

TABLE (2).

Data plotted in Curve (2).

Stearic Acid Mol %	Myristic Acid Mol %	Freezing Point °C.
100.0	0.0	69.1
89.7	10.3	67.2
80.2	19.8	65.1
70.1	29.9	62.5
59.9	40.1	59.5
50.4	49.6	56.2
48.7	51.3	55.4
42.8	57.2	52.7
36.9	63.1	50.4
29.9	70.1	48.4
25.9	74.1	47.7
21.8	78.2	46.35
18.8	81.2	46.6
16.4	84.6	46.9
12.8	87.2	48.0
8.4	91.6	49.3
4.2	95.8	51.2
0.0	100.0	54.1

TABLE (3).

Data plotted in Curve (3).

Stearic Acid Mols %	Lauric Acid Mol %	Freezing Point °C.
100.0	0.0	69.1
86.2	13.8	66.7
75.8	24.2	64.6
64.6	35.4	61.9
53.1	46.9	59.0
49.6	50.4	57.7
39.9	60.1	53.5
31.2	68.8	48.0
29.9	70.1	47.0
23.1	76.9	41.7
14.9	85.1	38.5
12.85	87.15	37.7
11.4	88.6	37.5
8.5	91.5	38.5
0.0	100.0	43.9

TABLE (4).

Data plotted in Curve (4).

Myristic Acid Mol %	Lauric Acid Mol %	Freezing Point °C.
100.0	0.0	54.1
89.1	10.9	51.2
76.5	23.5	47.3
65.0	35.0	43.3
52.8	47.2	38.0
48.9	51.1	36.75
44.5	55.5	36.7
38.7	61.3	36.2
32.1	67.9	35.2
27.2	72.8	34.0
22.9	77.1	34.7
17.3	82.7	36.55
10.1	89.9	39.4
0.0	100.0	43.9

TABLE (5).

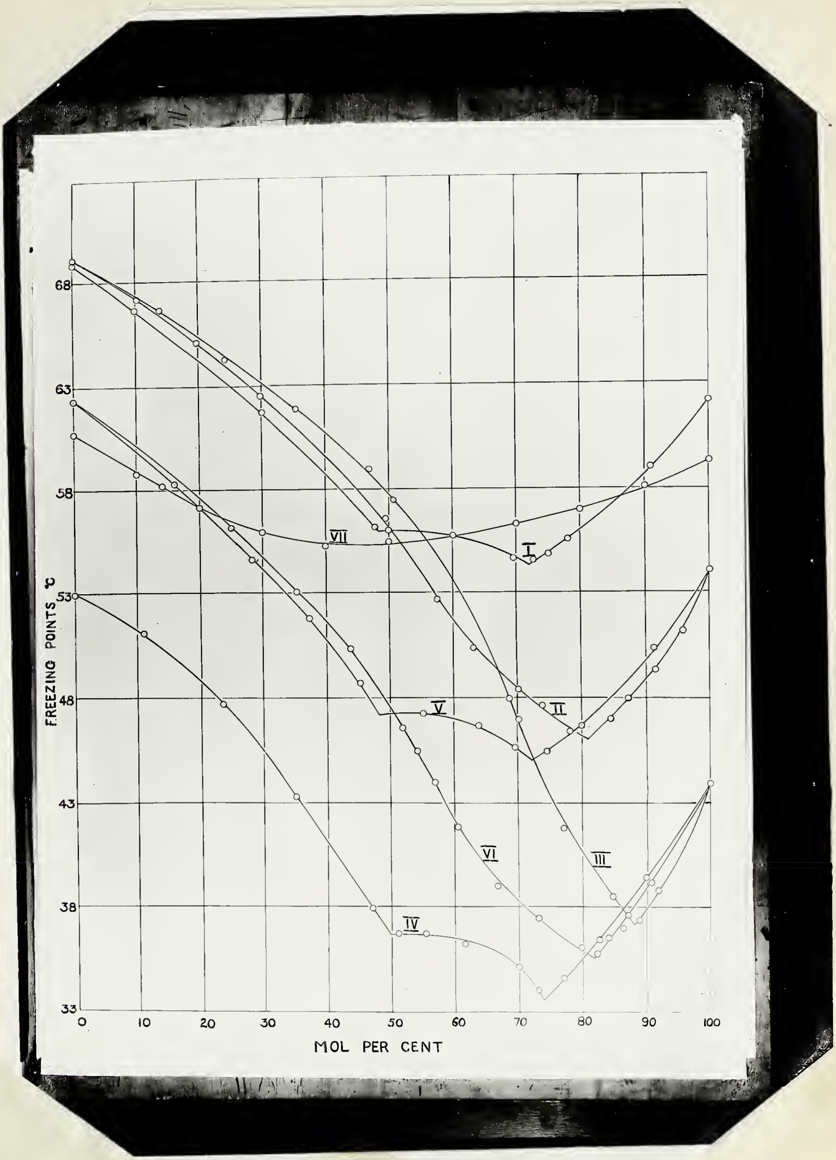
Data plotted in Curve (5).

Palmitic Acid Mol %	Myristic Acid Mol %	Freezing Point °C.
100.0	0.0	62.3
84.0	16.0	58.3
71.7	28.3	54.7
63.6	37.4	51.9
54.7	45.3	48.7
48.5	51.5	47.3
43.7	56.3	47.3
36.1	63.9	46.7
30.6	69.4	45.6
25.4	74.6	45.5
20.3	79.7	46.7
8.7	91.3	50.4
0.0	100.0	54.1

TABLE (6).

Data plotted in Curve (6).

Palmitic Acid Mol %	Lauric Acid Mol %	Freezing Point °C.
100.0	0.0	62.3
85.9	14.1	58.2
74.8	25.2	56.2
64.6	35.4	53.1
57.2	42.8	50.4
50.3	49.7	47.5
48.1	51.9	46.6
45.7	54.3	45.5
43.2	56.8	44.0
39.5	60.5	41.8
33.2	66.8	39.0
26.8	73.2	37.6
20.4	79.6	36.1
18.8	81.2	35.8
15.9	84.1	36.7
13.6	86.4	37.0
9.3	90.7	39.2
0.0	100.0	43.9


FREEZING POINTS °C
68
63
58
53
48
43
38
33
0
10
20
30
40
50
60
70
80
90
100
MOL PER CENT
I
II
III
IV
V
VI
VII

DISCUSSION.

Curve (1) which shows the freezing points of mixtures of palmitic and stearic acids, possesses a transition point which clearly indicates the formation of a compound. Since the compound decomposes at or near its melting point, it is difficult to state its exact composition, but it appears to be very close to an equimolecular mixture of the two fatty acids. The eutectic temperature for palmitic and stearic acids is 54.6° at a composition of 71.0 mol per cent of palmitic acid and 29.0 mol per cent of stearic acid. At the transition point and at the eutectic, the temperature, after crystallization was induced by supercooling, remained constant for a considerable time.

Curves (4) and (5) show the freezing points of mixtures of myristic and lauric, and palmitic and myristic acids respectively. The curves are of the same shape as Curve (1), both indicating clearly compound formation at an equimolecular mixture of the two acids. The eutectic temperature for myristic and lauric acids is 34.0° C at a composition of 74.0 mol per cent of

lauric acid and 26.0 mol per cent of myristic acid. The eutectic temperature for palmitic and myristic acids is 44.8° C at a composition of 71.0 mol per cent of myristic acid and 29.0 mol per cent of palmitic acid.

Curves (2) , (3) , and (6) show the freezing points of mixtures of stearic and myristic, stearic and lauric, and palmitic and lauric acids respectively. The curves are of an altogether different form. There is no transition point and therefore no compound formation. That there is no compound formation in these cases is further confirmed by studying the cooling curves. Since at the transition point a new compound is formed, a mixture of this composition will show a horizontal part of the curve (DE fig. 1) in the cooling curve, i. e. the mixture behaves like a pure substance. Experimentally no mixtures represented by Curves (2) , (3) , and (6) behaved as pure substances except mixtures at their eutectic points. Special care was taken in studying equimolecular mixtures of these fatty acids, but in each of these three mixtures of different fatty acids there was no evidence for compound formation. The eutectic

temperature for stearic and myristic acids is 46.3° C at a composition of 20.0 mol per cent stearic acid and 80.0 mol per cent myristic acid. The eutectic temperature for stearic and lauric acids is 37.5° C at a composition of 89.0 mol per cent lauric acid and 11.0 mol per cent stearic acid. The eutectic temperature for palmitic and lauric acids is 35.8° C at a composition of 81.0 mol per cent lauric acid and 19.0 mol per cent palmitic acid.

The binary system for palmitic and lauric acids has been done by P. Waentig and G. Pescheck[11] in 1919. They reported a transition point showing compound formation at an equimolecular mixture of the two fatty acids. It was observed that the melting points of the fatty acids that they used were about 1.5° C lower than the melting points of the fatty acids used in this work. Therefore the work for the binary system was repeated and there was no evidence for compound formation found. Special precautions were taken when working with this binary system. The error therefore in the work of Waentig and Pescheck may lie in the impurity of the fatty acids.

Curve (7)[5] represents the freezing points of

mixtures of palmitic and margaric acids. There is no eutectic temperature. The two fatty acids form a series of solid solutions. It would therefore be very difficult to separate two such fatty acids by recrystallization.

This work and the work of Shriner, Fulton, and Burke [5] shows that in the fatty acid binary systems, there are three types of curves. The type with a transition point and a eutectic (Curves (1), (4), and (5).), the type with a eutectic alone (Curves (2), (3)' and (6).), and the type with no eutectic and no transition point (Curve (7).). It is interesting to note that when the difference in the number of carbon atoms of the two fatty acids forming the binary system is one, we get a continuous curve. [5] (Curve (7).). When the difference in the number of carbon atoms is two, then the curve consists of a transition point and a eutectic. (Curves (1), (4), and (5).). When the difference in the number of carbon atoms is four or six, then the curve has a eutectic alone. (Curves (2), (3), and (6).). It would be interesting to try out binary systems of odd numbered carbon atom fatty acids to see if the behavior is the

same as with the even numbered carbon atom fatty acids.

The relationship between the melting points of the pure acids, compounds, and mixtures is shown in Tables (7) and (8).

TABLE (7).

CAPILLARY MELTING POINTS.

	Soften At° C.	Liquid At°C.	
1. Pure Stearic acid	69.3	69.5	
2. Pure Nondecylic acid		66.0	[13]
3. Pure Palmitic acid	62.6	62.9	
4. Pure Margaric acid	59.9	60.0	[5]
5. Pure Pentadecylic acid		54.0	[13]
6. Pure Myristic acid	54.5	54.8	
7. Pure Tridecylic acid		51.0	[13]
8. Pure Lauric acid	44.1	44.3	
9. Pure Undecylic acid		29.3	[13]
10. Pure Decylic acid		31.0	[13]

TABLE (8).

FREEZING POINTS OF COMPOUNDS AND MIXTURES.

	Freezing Point ° C.
1. Equimolecular mixture of stearic and palmitic acids	56.2
2. Eutectic of stearic and palmitic acids	54.6
3. Eutectic of stearic and myristic acids	46.3
4. Eutectic of stearic and lauric acids	37.5

5. Equimolecular mixture of palmitic and myristic acids	47.3
6. Eutectic of palmitic and myristic acids	44.8
7. Eutectic of palmitic and lauric acids	35.7
8. Equimolecular mixture of myristic and lauric acids	36.8
9. Eutectic of myristic and lauric acids	34.0

Cooling curves in the determination of the criteria of purity of fatty acids have their limitations in the fact that compounds and eutectics behave as pure substances. It is clearly seen from Tables (7) and (8) how the eutectic mixture of stearic and palmitic acids may be mistaken for myristic acid, also the equimolecular mixture of palmitic and stearic for margaric acid. The freezing points of the mixtures will be a few degrees lower than the capillary melting points.[5] An equimolecular mixture of palmitic and myristic acids may be easily mistaken for tridecylic acid. Other similar examples may be found in the tables. Therefore the cooling curve or melting point is not conclusive enough evidence for the purity of a fatty acid. In such cases, the neutral equivalents as described in the previous

paper are more conclusive evidence for the purity of fatty acids.

CONCLUSION.

Binary systems of some fatty acids have been studied. It was found that binary mixtures of stearic and palmitic, palmitic and myristic, and myristic and lauric acids show a transition point and a eutectic point. Binary mixtures of stearic and lauric, stearic and myristic, and lauric and palmitic acids show only an eutectic point and no transition point.

PART THREE.

THE PREPARATION AND DECOMPOSITION OF p-METHOXY-PHENYL o-CHLORO-PHENYL IODONIUM BROMIDE: A METHOD OF ESTABLISHING THE RELATIVE DEGREE OF ELECTRONEGATIVITY OF ORGANIC RADICALS.

A study of the electronegativity of organic radicals is of much importance from the standpoint of the electronic conception of valence. The information can also be used advantageously in the interpretation of a number of baffling organic reactions.

There are various means employed for representing the carbon to carbon linkages. Among them are the Kekule bond, the polar bond, the Stark-Lewis bond, and Kharasch's extension of the Stark-Lewis idea. The theory of valence advanced by Lewis [14] points the way to fruitful representation of a carbon to carbon linkage. It is the basis of the Lewis concept that two electrons lying between the two atomic nuclei, constitute the chemical bond, and that the pair of electrons may be so placed with reference to the two nuclei as to give rise to no electrical polarization, or may be displaced in the

direction of one nucleus or the other to give to the one atom a negative charge and to the other a positive charge. These possibilities are indicated by Lewis in the following manner:

(1) $A \quad : \quad B$ (2) $A \qquad : B$ (3) $A : \qquad B$

In any case it is to be considered that the atoms A and B continue to share the bonding pair, and that only in the extreme case exemplified by an ionizing compound does one atom completely capture the pair at the expense of the other.

Electronegativity of a radical is defined as the affinity of that radical for the pair of valence electrons. The attraction of the radical for the pair of valence electrons is a function of the electronic structure of the molecule, and thus arises the difference of electronegativity of organic radicals. In order to make effective use of this concept it is necessary to devise some means of determining the relative electronegativities of organic radicals. That accomplished, we would have at hand a table comparable in utility to the

"electromotive series" which systematized the early chaos of inorganic chemistry. It is obvious, that since in dealing with radicals which, for the most part, are incapable of becoming ions, that the elegantly exact quantitative method of determining inorganic electronegativities, is inapplicable to organic radicals.

Kharasch and Sher [15] extend the Lewis concept. As will be seen, numerous variations of the types of union indicated by Lewis are possible. These possibilities may be expressed most conveniently in terms of the Bohr concept of electronic energy levels.

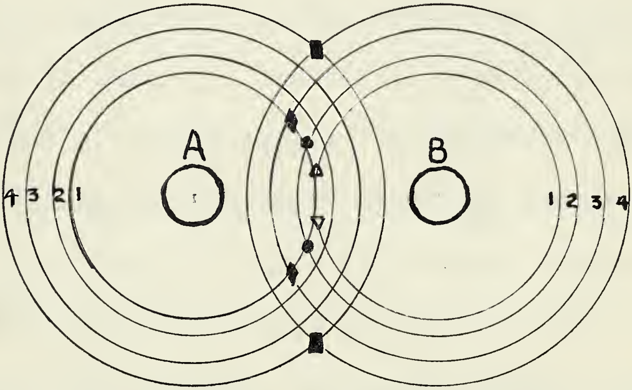


Fig. 1.

The two carbon atoms can share a pair of electrons at the intersection of their inner shells (corresponding presumably to bond (1) of Lewis), or at the intersection of inner shell (1) of one and the outer shell (4) of the other, thus leading to polarization, or the reverse may be true. It is however also conceivable that the pair of valence electrons may be shared in the outer layers of the two carbon atoms, namely shell (4) of one and shell (4) of the other, as denoted by the dark rectangles of Fig. 1.

Undoubtedly, two atoms or radicals that share a pair of valence electrons in their outer shells have a very slight attraction for the electrons, consequently the compound is unstable. The figure only indicates sufficient number of energy levels to illustrate conveniently the concept of Kharasch. Electrons shared in the first energy levels of A and B (1,1 energy levels) constitute a non-polar and highly stable bond. It is typical of compounds like diphenyl. Electrons shared in the second energy levels of A and B (2,2 energy levels) constitute a strictly non-polar bond. This is however, less

stable than the first one discussed. Ethane may be cited as an illustration. Electrons shared in the third and fourth energy levels respectively, are also non-polar, but represent successively decreasing degrees of stability. These illustrations demonstrate that the primary criteria of stability of a carbon to carbon bond is not its polarity or non-polarity, but the affinity of the bound radicals for the binding electrons.

Now consider that A represents a radical capable of extreme electronegativity (such as the chloride) and that B represents an organic radical. We may then say, that the black circles (1 energy level of A and 2 energy level of B) represent an electron pair shared by a chloride radical and a highly electronegative organic radical such as the phenyl or naphthyl radical. The white circles (1 energy level of A and 3 energy level of B) represent an electron pair shared by a chloride and a moderately electronegative organic radical such as methyl. The diamonds (1 energy level of A and 4 energy level of B) represent a bonding pair of electrons shared by a chloride and a weakly electronegative organic radical such as

the triphenyl methyl. These bonds increase in the degree of polarity in the order named. The bonds decrease in stability as the degree of polarity increases. It may be stated that a low degree of affinity for electrons (i.e. electronegativity) on the part of a radical results in instability of the bond which that radical may form with another radical or atom, regardless of the polarity of the bond thus formed.

METHOD OF ESTABLISHING RELATIVE ELECTRONEGATIVITIES OF ORGANIC RADICALS.

Kharasch and Grafflin,[16] Kharasch and Marker,[17] Kharasch and Reinmuth,[18] and Kharasch and Reinmuth [19] established experimentally the relative electronegativities of many organic radicals. Their method of approach was by coupling two organic radicals R' and R'' whose electronegativity was to be compared, with bivalent mercury and then treating with hydrochloric acid. The following equation represents the reaction:

$$R'HgR'' + H^{+}Cl^{-} \longrightarrow R'HgCl + R''H.$$

The more electronegative of the two radicals, R' and R'',

combines with H^+ to form the corresponding hydrocarbon. Thus by identifying the products of decomposition, the relative electronegativity of organic radicals R' and R'' is established. The above mentioned workers compared the electronegativities of many radicals and from their work drew up a table of decreasing electronegativities of organic radicals.

In this work, an attempt has been made to establish the relative electronegativity of organic radicals by an altogether different method of approach. The two organic radicals R' and R'', are coupled with an iodonium bromide radical, and then decomposed. The following reaction takes place:

$$\begin{matrix} R' \searrow \\ \quad\;\; I-Br \\ R'' \nearrow \end{matrix} \xrightarrow{\text{heat}} R'I + R''Br.$$

Here it is plausible to assume that the bromine being itself highly electronegative will go to the organic radical which is less electronegative of the two. Thus if R'' is less electronegative than R', then on heating the compound R'R''IBr, we should get R'I and R''Br.

The purpose of this investigation therefore, was first, to prepare the compound R'R''IBr, and secondly, to decompose it, and examine the products of decomposition, thus confirming the order of electronegativity of the organic radicals as established by Kharasch and his collaborators.

Hartman and Meyer [20] and Willgerodt [21] have prepared symmetrical iodonium compounds by allowing equimolecular mixtures of the iodoxy-benzene and iodoso-benzene to react with moist silver hydroxide. In this work an unsymmetrical iodonium compound was prepared in the same way.

EXPERIMENTAL.

Preparation of p-Methoxy-phenyl Iodide. [22]

One gram molecular weight of anisidine was treated with two and one half gram molecular weights of hydrochloric acid. After cooling the mixture to 0°C , the solution was diazotized with one gram molecular weight of sodium nitrite, and then treated with one gram molecular weight of potassium iodide. The solution was

warmed, and when the evolution of gas was complete, it was made alkaline and then steam distilled. The oily layer in the distillate was separated, dried, and distilled. The distillate, on cooling, solidified to a pale brown cake.

Preparation of p-Methoxy-iodoso-benzene.

The p-methoxy-phenyl iodide was dissolved in four times its weight of chloroform, cooled, and chlorine gas passed into it. The solid p-methoxy-phenyl iodide dichloride which separated, was filtered off, and treated with a solution of sodium hydroxide immediately. (4 g. of water and .5 g. of sodium hydroxide for every gram of p-methoxy-phenyl iodide dichloride.) It was found that the p-methoxy-phenyl iodide dichloride is very unstable and therefore, immediate treatment with sodium hydroxide is necessary. After allowing to stand in contact with sodium hydroxide overnight, the p-methoxy-iodoso-benzene was filtered off and washed free of sodium hydroxide.

Preparation of p-Methoxy-iodoxy-benzene.

The p-methoxy-iodoso-benzene was formed into

a thick paste with water and then steam passed into it. Some p-methoxy-phenyl iodide distilled over with steam, while the p-methoxy-iodoxy-benzene remained behind as an orange solid. Enough hot water was added to dissolve the orange solid. On cooling the feathery p-methoxy-iodoxy-benzene came down. The yield was low.

Preparation of o-Chloro-phenyl Iodide.

The o-chloro-phenyl iodide was prepared from o-chloro-aniline by diazotization, and treatment with potassium iodide as described in the preparation of p-methoxy-phenyl iodide. The o-chloro-phenyl iodide distilled over at ~~204~~ 229°C as a brown colored liquid.

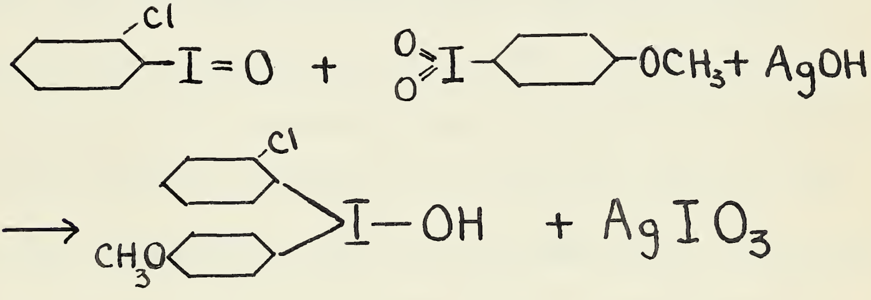
Preparation of o-Chloro-iodoso-benzene.

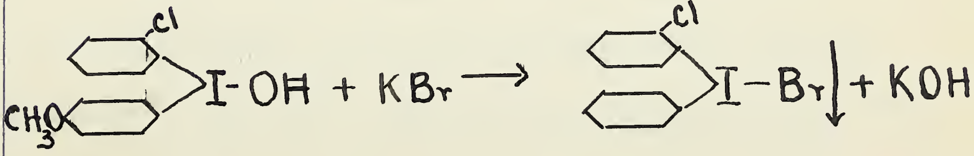
The o-chloro-iodoso-benzene was prepared from the o-chloro-phenyl iodide going through the o-chloro-phenyl iodide dichloride as described in the preparation of p-methoxy-iodoso-benzene.

Preparation of p-Methoxy-phenyl o-Chloro-phenyl Iodonium Bromide.

Equivalent quantities of p-methoxy-iodoxy-

benzene, o-chloro-iodoso-benzene, and freshly prepared silver hydroxide were well mixed. The o-chloro-iodoso-benzene was added in slight excess. To the mixture a few cc. of chloroform, and water, was added. The mixture was shaken well in a stoppered flask and allowed to stand for twenty-four hours. The liquid was filtered off, several water extractions from the residue made, and the combined filtrate treated with potassium bromide. A white flocculent precipitate resulted. The p-methoxy-phenyl o-chloro-phenyl iodonium bromide was recrystallized from water. The following reactions take place:





THE DECOMPOSITION OF p-METHOXY-PHENYL o-CHLORO-PHENYL IODONIUM BROMIDE, AND THE IDENTIFICATION OF THE PRODUCTS OF DECOMPOSITION.

The dry p-methoxy-phenyl o-chloro-phenyl iodonium bromide was heated in a test tube in an arochlor bath. Decomposition was quite sharp at 165°C. The whole mass became a dark colored liquid. The products of decomposition were then identified. The dark colored liquid was distilled, obtaining two fractions, one at 200 - 210°C, the other at 210 - 235°C. The second fraction solidified on cooling, but the first remained a liquid. The solid fraction was recrystallized from alcohol and the melting point of the product was 49°C, that of pure p-methoxy-phenyl iodide is 50°C. Then a mixture of pure p-methoxy-phenyl iodide and the purified second fraction was made and the melting point of the mixture determined. There was no lowering of the melting point indicating that the two compounds were the same. The boiling points recorded in the literature of p-methoxy-phenyl iodide and o-chloro-phenyl bromide are 237°C and 204°C respectively. This is further evidence for the compounds. At present, still further work

is being done to confirm the products of decomposition. The yield of the p-methoxy-phenyl o-chloro-phenyl iodonium bromide was small, and it was necessary to work on a micro scale.

CONCLUSIONS.

The compound p-methoxy-phenyl o-chloro-phenyl iodonium bromide has been prepared. From the work that has been done so far, evidence points in the direction to confirm the findings of Kharasch and his collaborators.

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